

Polymeric flocculants based on the interfacial characteristics of fine clay minerals: A review

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Abstract: Fine clay minerals, found in various industrial effluents, have attracted much attention in recent times. They can form a highly stable suspension in water and increase the complexity of sedimentation for the treatment of wastewater. In the past few decades, the flocculation of fine clay minerals has been significantly improved due to numerous design advancements in the molecular weight, charge density and structure of polymeric flocculants. In this article, the interfacial characteristics and affecting factors of clay minerals are discussed, the design, synthesis and application of synthetic polymers, natural polymers and natural-based grafted polymers are reviewed, as well as the advantages and disadvantages of three types of polymers. The development direction of upgrading existing clay mineral flocculants is proposed based on the interfacial characteristics of clay minerals. Weakening the hydration of clay minerals, altering the manner of molecular interaction and precisely controlling the structure of polymer chains are the design objectives of novel polymeric flocculants.

Keywords: clay minerals, interfacial characteristic, polymer, flocculation

1. Introduction

With the development of industrial technology and the improvement of mechanization, a large number of clay minerals exist in various industrial effluents such as papermaking, beneficiation, coal tailings, mineral processing and sludge dewatering (Feng et al., 2020; Zhou et al., 2016). In the case of coal tailing, data shows there are about 30wt.% clay minerals in original tailings and 30-50 wt.% in mature fine tailings (Botha and Soares, 2015; Sabah et al., 2004). In the coal slurry water, there are different kinds of fine clay particles at less than 2 μm dispersed in water, including kaolinite, montmorillonite and illite, which produce a highly stable clay-water suspension, making it difficult to agglomerate and clarify (Chen et al., 2019a; Min et al., 2018; Ndlovu et al., 2013). Ignoring these dispersions without appropriate treatment will not only waste precious water but also lead to serious environmental problems, which is not in line with the concept of sustainable development. For this reason, it is significant and challenging to remove fine clay mineral particles from industrial wastewater.

Numerous technologies have been devised to treat fine clay particles, including physical, chemical and biological methods. It emerged that coagulation and flocculation are efficient methods to separate suspended particles in industrial wastewater. With the addition of a coagulant or flocculant, the dispersed fine clay particles are aggregated to form larger flocs, and the system becomes clear after precipitation (Ezzahra Aboussabiq et al., 2014). Coagulation is the process of overcoming the impulsive energy barrier between particles by increasing the ionic strength. It generally works by introducing inorganic metal salt ions such as polymerized ferrous sulfate, aluminum sulfate and aluminum chloride, which all play important roles in charge neutralization and compression of the

electric double layer (Jiao et al., 2015; Lee et al., 2012). However, the wide range of utilization of coagulation has been limited since its toxicity of the high metal (e.g., aluminum) concentration in the treated water, large dosage, inefficiency and narrow application (Lee et al., 2014). In contrast, flocculation technology is more conducive to facilitating the separation process of fine clay suspension (Pal et al., 2012; Sharma et al., 2006). In the past few decades, it has emerged three types of polymeric flocculant, which are synthetic polymers, natural polymers and natural-based grafted polymers (Salehizadeh et al., 2018).

Although much research has been done on the performance of polymeric flocculants, there are still some deficiencies in these flocculants. In this article, firstly, the interfacial characteristics and affecting factors of clay minerals are introduced in detail. The interface of different clay minerals varies greatly in aqueous solutions. Only by deeply understanding the interfacial characteristics of clay minerals can we accurately optimize the design of novel polymeric flocculants. Secondly, a comprehensive overview of synthetic polymers, natural polymers, and natural-based grafted polymers based on the intrinsic characteristics such as molecular weight, charge density, and spatial configuration and the synthetic technique are summarized. Meanwhile, the advantages and disadvantages of the three kinds of polymers are compared. Finally, we propose the development direction of efficient polymeric flocculants based on their interfacial characteristics. This article can help practitioners rapidly and effectively comprehend the state of research on polymeric flocculants used in the treatment of clay minerals, as well as the future development direction of flocculants.

2. Interfacial characteristics of clay minerals

Clay minerals are typical phyllosilicates and their structural units are Al-O octahedron ($[AlO_6]$) and Si-O tetrahedron ($[SiO_4]$), which are usually classified into 1:1 (T-O) and 2:1 (T-O-T) structures. A 1:1 phyllosilicate is composed of one tetrahedral silica layer and one octahedral alumina layer, while a dioctahedral 2:1 phyllosilicate comprises two tetrahedral silica layers together with one octahedral alumina layer. The crystal of both T-O and T-O-T minerals is often accompanied by lattice defects and lattice substitution, such as Al^{3+} is substituted by Fe^{2+} in the octahedral sheet of T-O clay mineral (Chen et al., 2020a), Si^{4+} is substituted by Al^{3+} in the tetrahedral sheet and Al^{3+} is substituted by Mg^{2+} in the octahedral sheet of T-O-T clay mineral (Carla G. Fonseca et al., 2016) (Fig. 1). Typical T-O and T-O-T structural clay minerals are listed in Table 1, among which kaolinite is the representative of T-O structural clays while montmorillonite and illite are the representatives of T-O-T structural clays.

Lattice substitutions or lattice defects cause a series of changes in the interface properties of clay minerals, and cation exchange capacity (CEC) is one of them, which has a significant effect on the characteristics of clay minerals. The higher the lattice substitution degree of clay minerals, the greater the CEC. Therefore, montmorillonite has a higher CEC than kaolinite and illite due to more isomorphous replacement in the lattice (Helling et al., 1964). The results of ion exchange adsorption affect the ability of clay particles to adsorb flocculants and change the dispersion and hydration characteristics of clays in an aqueous solution (Parfitt et al., 1995). Moreover, the surface polarity of clays is increased with the lattice substitution, and the stability of the hydrated film on the clay surface is enhanced (Atluri et al., 2019).

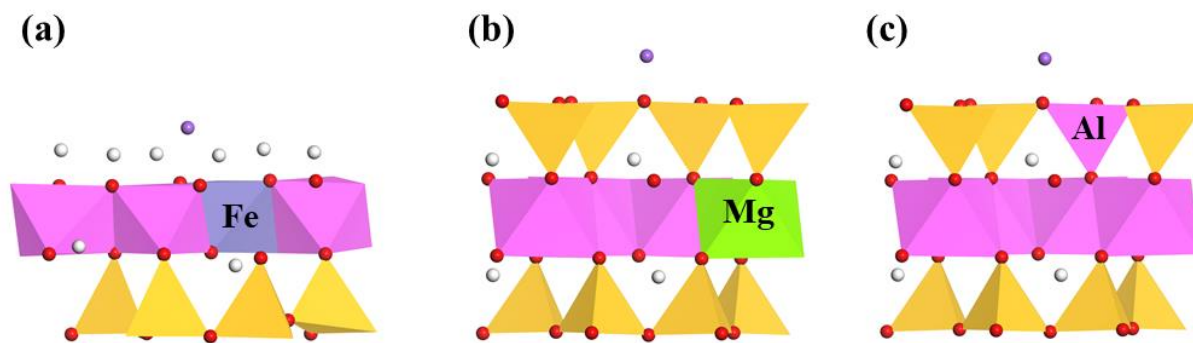


Fig. 1. The lattice substitution of clay minerals. (a) Fe replaces Al in T-O clay mineral; (b) Mg replaces Al in T-O-T clay mineral; (c) Al replaces Si in T-O-T clay mineral

Table 1. Typical clay minerals with T-O and T-O-T structures

Clay Structure	Representative clays
T-O	kaolinite, halloysite
T-O-T	montmorillonite, illite, pyrophyllite, chlorite, muscovite, sepiolite

2.1. Effect of water on interfacial characteristics

As we all know, clay minerals with either T-O or T-O-T structure are hydrated in aqueous solutions due to their strong hydrophilicity. Our previous studies have proven that three water layers with a total thickness of 8-10Å are formed on the surface of clay mineral particles in solutions (Min et al., 2018). The first water layer closest to the particle is called "structural water", the third water layer far from the particle is the bulk water, and the middle layer is the transition layer (Fig. 2). Moreover, the density and viscosity of water in the hydrated film are higher than that of water in bulk phase (Peng and Min, 2015; Chen et al., 2019b). The water densities of the three layers of hydration film from inside to outside on the kaolinite (001) surface are 1.56 g/cm³, 1.19 g/cm³ and 1.02 g/cm³, respectively (Ren et al., 2021). The densities of water on the quartz (001) surface are 1.83 g/cm³, 1.26 g/cm³ and 1.07 g/cm³, respectively (Liu et al., 2019a). The increase of density and viscosity in hydration film restricts the flocculant molecules from attaching to clay minerals surfaces. Therefore, it is the crucial factor affecting the agglomeration and settlement of fine clay particles in wastewater, and flocculants with strong interaction with clay minerals are urgently needed.

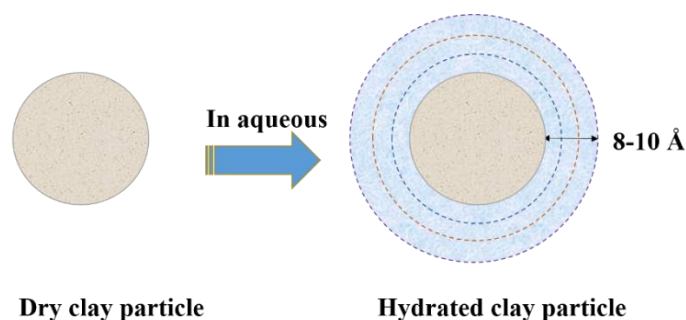


Fig. 2. Schematic diagram of hydrated film on clay mineral surface. (Peng and Min, 2015)

In general, clays with a T-O-T structure are more challenging to settle than the T-O structural clays (Ma et al., 2018). For instance, montmorillonite is more challenging to aggregate owing to the strong hydration behaviour and osmotic swelling by adsorbing water molecules on the surface and interlayer of montmorillonite in aqueous solutions. Conversely, the strong hydrogen bonding between layers of kaolinite prevents water from penetrating the interlayer space, and thus kaolinite reveals little swelling behaviour in solutions (Min et al., 2015; Peng et al., 2016; Zhang and Peng, 2015).

2.2. Effect of pH on interfacial characteristics

The pH of a solution is an essential factor affecting the flocculation of clay minerals, which is directly related to variable charges occurring on clay particles' edge surfaces. A permanent negative charge is formed on the basal surface. The edge surface may be positive or negative depending on Al-OH and Si-OH adsorbing hydrogen and hydroxyl ions in different pH solutions (Nakamura and Murakami, 2019; Tombácz and Szekeres, 2004). For montmorillonite, when the pH value is lower than 6.5, the edge Al-OH site is protonated to produce a positive charge. When the pH level increases, the deprotonation reaction occurs at the Si-OH and Al-OH sites, resulting in a negative charge at the edge (Tombácz and Szekeres, 2004).

This unique structure means that different pH of solution causes the suspension system containing clay particles to flocculate or stabilize. Wilkinson et al. reported that the structure of bentonite aggregates was dominated by the edge surfaces at low pH, whereas the structure was dominated by the basal surfaces at high pH (Wilkinson et al., 2018). Furthermore, the zeta potential is changed by varying pH values. When the pH is low, some of the negative charges on the clay particles

are neutralized by adding acid to provide more H^+ ions to the solution. Increasing the pH leads to raising the zeta potential of clay particles and intensity of electrostatic repulsion between clay particles, thus enhancing the stability of suspension (Fig. 3) (Chang et al., 2009; Konduri and Fatehi, 2017). Practice shows that the pH of industrial wastewater often changes dynamically, affecting the effect of flocculants, so a more adaptable flocculants are needed, that is, flocculants that can stabilize flocculation in a wide pH range.

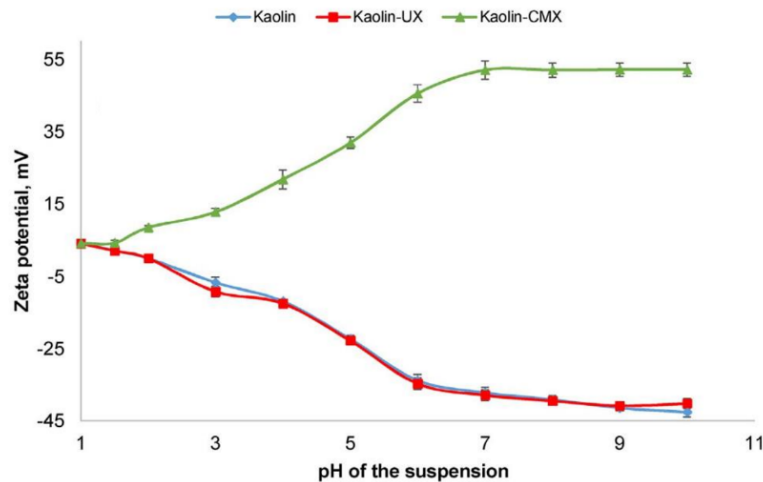


Fig. 3. Effect of zeta potential of kaolinite at different pH suspensions (Konduri and Fatehi, 2017)

2.3. Effect of metal cations on interfacial characteristics

Due to the complexity of clay mineral wastewater systems, the composition of metal cations contained in the wastewater is different, which has an influence on the interfacial properties of the clay minerals. Li et al. (Li et al., 2020) has reported that the interfacial distribution of cations changes compared with the outer surface of clay minerals when metal cations are present in the solution. The surface wettability of clay minerals with a T-O-T structure is also affected by the exchangeable cations (Yi et al., 2018). Furthermore, metal cations can affect the thickness of hydration film on the surface of clay particles. Generally, the thickness of hydration film decreases with the increase of metal cation concentrations, while Na^+ and K^+ are beneficial to the formation of hydration film at low concentration. The decreasing order of zeta potential of kaolinite by different metal cations is $Al^{3+} > Mg^{2+} > Ca^{2+} > K^+ > Na^+$ (Min and Zhao, 2013). Therefore, the type and concentration of ions in the solution can affect the effect of flocculants.

3. Advancements in polymeric flocculants for clay minerals

Flocculation is a process in which fine particles are destabilized and collide with each other to form aggregates (flocs). The optimum dosage of flocculant is about the amount of polymer required to make the particle charge close to zero. Excessive polymer can make the particles charged and stabilized again, resulting in the increase of viscosity and dispersion of the suspension. In this case, the biggest impact on the performance of the polymer is the charge density (generally high charge density is more effective), while the molecular weight of the polymer has little impact on its performance. Therefore, selecting or designing an optimal flocculant is critical to the efficient treatment of clay minerals (Gregory and O'Melia, 1989). An ideal flocculant should be inexpensive, easily obtained, non-toxic, pH-dependent and biodegradable. However, there is no flocculant that can satisfy all these conditions simultaneously. In recent years, many researchers have developed three types of flocculants, namely, synthetic polymers, natural polymers and natural-based grafted polymers. In order to clarify the wastewater containing fine clay particles, previous studies have been undertaken to study the influence of polymeric flocculants with varying molecular weight, charge density and spatial structure on the settling behaviour and flocculation characteristics of clay minerals (Bárány et al., 2011; Guo et al., 2019) (Fig. 4).

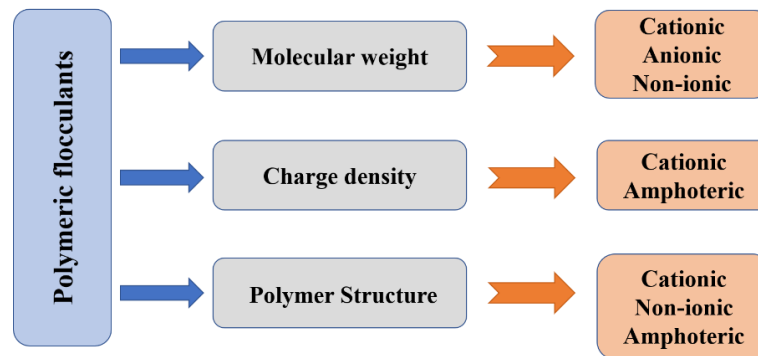


Fig. 4. Intrinsic properties and corresponding types of polymeric flocculants

3.1. Synthetic polymers

Synthetic organic flocculants have been used to remove clay minerals for a long time due to their remarkable flocculating ability. They are prepared mostly by free radical polymerization, enabling the flocculants to have molecular weights in the millions and form large aggregates at low dosages. Polyacrylamide (PAM) has been explored for several decades. It has become the first commercial polymeric flocculant for industrial wastewater, which can be classified into four categories: cationic, anionic, amphoteric and non-ionic PAM. All four types of PAMs have been reported to be used to treat wastewater containing clay minerals. The commercial PAMs do not eliminate the effects of hydration and require flocculation within a narrow pH range.

3.1.1. Cationic synthetic polymers

Cationic flocculants contain positively charged groups, typically quaternary ammonium functional groups such as 2-acryloyloxyethyl trimethyl ammonium chloride (DAC), 2-methacryloyloxyethyl trimethyl ammonium chloride (DMC), diallyl dimethyl ammonium chloride (DADMAC), 2-methacrylamidopropyl trimethyl ammonium chloride (MAPTAC), and 3-acrylamidopropyl trimethyl ammonium chloride (ATMAC). They are the most common monomers copolymerized with acrylamide (AM) to produce cationic PAM for flocculation because they have rich active groups such as C=C, -COO-, -CONH₂.

It is known from the structure that clay minerals are negatively charged in wastewater, while cationic polymeric flocculants can combine strongly with these particles. The mutual attraction of opposite charges reduces charges on the surface of fine clay mineral particles and the result is the reduction of electrostatic repulsion between the particles. In this case, the charge density and zeta potential of the clay particles are diminished, resulting in destabilization of the system (Lou et al., 2017). Simultaneously, the quantity of particles adsorbed by polymers is affected by the charge density of polymers. In principle, the higher the charge density of polymers, the greater the amount adsorption of particles within a certain range. The charge density of cationic copolymers is a critical factor for clay minerals flocculating. An increase in the charge density of cationic polymers will enhance their adsorption onto clay minerals (Chen, 1998).

3.1.2. Anionic synthetic polymers

Anionic flocculants contain negatively charged groups that are usually attributed to carboxylic or sulfonic acids such as acrylic acid (AA), styrene sulfonic acid (SSA) and 2-acrylamide-2-methylpropane sulfonic acid (AMPS). Anionic flocculants with high molecular weight are frequently used in the settling and clarifying of negatively charged clay minerals. For instance, the use of high molecular weight anionic polyacrylamide (APAM) in flocculating negatively charged particles is more efficient than cationic polymers to some extent by increasing the settling rate and forming a specific structure. It can also avoid the solidification of negatively charged clay particles caused by excessive adsorption of the polymer driven by strong electrostatic attraction (Nasser and James, 2006). In some

systems, divalent metal cations (e.g., Ca^{2+}) can act as a complexing agent between anionic polymer sites and negatively charged clay particles (Bolto and Gregory, 2007).

3.1.3. Amphoteric synthetic polymers

Amphoteric flocculants possess both cationic and anionic functional groups, which are used to remove positively and negatively charged colloid particles simultaneously. The composition of mineral processing wastewater containing clay minerals is complex, including negatively charged clay particles and positively charged metal cations. Even when clay minerals are of the same type, the surface charge varies with different pH values in an aqueous solution. The most common amphoteric polymeric flocculants are synthesized by copolymerizing quaternary ammonium functional groups with carboxylic acid or sulfonic acid.

3.1.4. Non-ionic synthetic polymers

Non-ionic flocculants lack ionizable functional groups in their chains. When the polymers contain less than 1% of charged functional groups, they would be generally considered as non-ionic polymers. The commonly used non-ionic flocculants rest on PAM, polyethylene oxide (PEO), or polyvinyl alcohol (PVA). PEO with high molecular weight can form a linear structure through the catalytic polymerization of ethylene oxide, and PVA is consisted of a copolymer of vinyl alcohol and vinyl acetate, respectively. The adsorption of PEO and PVA chains can occur between -O- and -OH groups (Al-OH or Si-OH) on the surface of clay minerals (Lapointe and Barbeau, 2020). Increasing the molecular weight of non-ionic polymers usually results in a larger hydrodynamic size and a better bridging effect (Chang et al., 2021).

3.1.5. Synthesis and application of synthetic polymers

Compared to anionic and non-ionic polymeric flocculants, cationic polymeric flocculants are preferred due to clay particles being negatively charged, and they can minimize the electronegativity of clay particles. In the study by Ma et al. (Ma et al., 2017b), a CPAM flocculant was polymerized with AM, DMDAAC and coconut diethanolamine (CDEA) utilizing low-pressure UV initiation (Fig. 5). Flocculation performance was tested for high turbid kaolinite suspension. Results showed that the intrinsic viscosity achieved 1577 ml/g, and the transmittance of kaolinite suspension reached 82.12-86.64% within the pH range of 2-10 and 1.5 mg/L dosage. The use of low-pressure UV can avoid high temperature and expensive equipment cost. Results unveiled that low-pressure UV irradiation can reduce activation energy of the polymerization and accelerate molecular bond breakage.

In a recent report by Sun et al. (Sun et al., 2021a), UV initiation polymerization technology helped to prepare cationic flocculant P(DAC-MAPTAC-AM) for coal chemical wastewater flocculation. The monomers ratio (DAC: MAPTAC: AM) and other conditions for synthesis were investigated. Results showed that the optimal dosage of P(DAC-MAPTAC-AM) was 8-12 mg/L at the pH range of 2-6, and the removal efficiency of turbidity was 81.0%. In addition, photoinitiation polymerization is an effective method which requires low activation energy and commences quickly at room temperature. Because only a small amount of photo initiator is used, the polymer with high purity, excellent solubility and stable performance can be obtained easily.

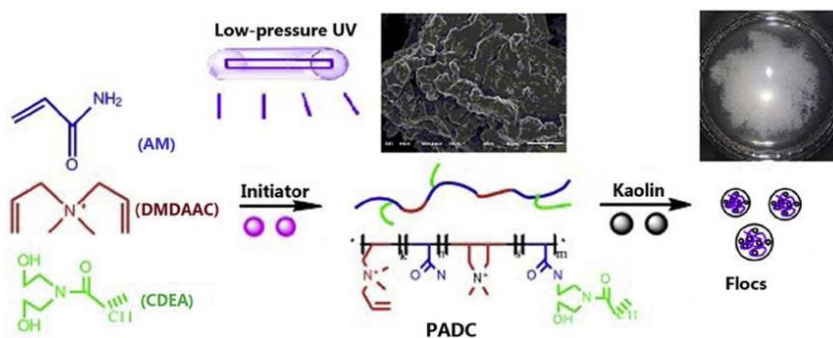


Fig. 5. Synthesis of a cationic polymeric flocculants (PADC) (Ma et al., 2017b)

An anionic flocculant was reported by Zhang et al. (Zhang et al., 2019), which was prepared by ultrasonic initiation method using AM, sodium styrene sulfonate (SSS) as monomers and poly (allylammonium chloride) as template (Fig. 6). The polymer structure was controlled through self-assembly and anionic monomers are more closely arranged, resulting in higher turbidity removal rate and lower zeta potential. Moreover, ultrasonic initiation could improve the collision of anionic oligomer with AM monomer, which has a synergistic effect with template copolymerization for flocculation. It was claimed that ultrasound can produce a “cavitation effect” in aqueous solutions, which promoted the rapid decomposition of molecules into free radicals and effectively triggered the polymerization process (Zhou et al., 2020). The effects of several typical synthetic flocculants used for removing clay minerals are tabulated in Table 1.

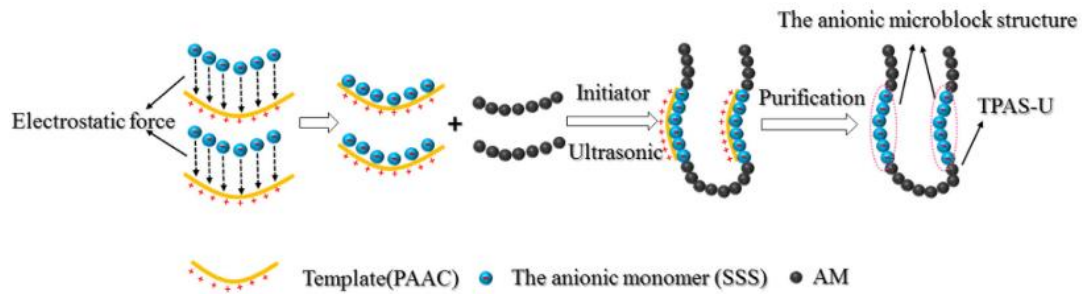


Fig. 6. Synthesis of an anionic polymeric flocculants (Zhang et al., 2019)

Table 2 The performance of representative organic synthetic flocculants

Flocculants	Type of flocculants	Flocculation medium	Reference
P(AM-DMDAAC-CDEA)	Cationic	Kaolinite	(Ma et al., 2017b)
P(AM-DAC-MAPTAC)	Cationic	Coal wastewater	(Sun et al., 2021a)
P(AM-DMDAAC)	Cationic	Clay particles	(Liao et al., 2017)
P(AM-DMC)	Cationic	Kaolinite	(Abdollahi et al., 2011)
P(AM-DMC)	Cationic	Kaolinite	(Ma et al., 2017a)
P(MA-AA)	Anionic	Clay suspensions	(Lu et al., 2014)
P(AM-SSS)	Anionic	Clay particles	(Zhang et al., 2019)
PAM	Non-ionic	Illite	(Wang et al., 2020b)

3.2. Natural polymers

Although synthetic flocculants exhibit high efficiency in removing solids, they also cause potential secondary pollution during flocculating due to the toxicity of residual monomer. Natural polymers have been proposed because they have some advantages such as non-toxic, biodegradable, inexpensive and produced from renewable materials since 1990s. Thus, chitosan, cellulose, starches, xylan, sodium alginate and cyclodextrin that are derived from plants and seaweeds have been emerged, and they are expected to be an alternative to traditional synthetic polymers (Anthony and Sims, 2013; Diaz-Barrera et al., 2014; Kaur and Dhillon, 2014; Wang et al., 2020a)

Commercial chitosan has a medium molecular weight and its charge density varies with the pH of the solution. Chitosan becomes positively charged due to the protonation of amino group in an acidic condition, and adsorb negatively charged clay mineral particles by electrostatic neutralization (Jaafari et al., 2004). Cellulose is insoluble in water, while carboxymethyl cellulose is water-soluble and can be used as a flocculant, which is a kind of anionic polymer (Barba et al., 2002). Starch is divided into amylose and amylopectin, amylose presents linear structure, while amylopectin is branched structure. In contrast, amylopectin has higher molecular weight and its branched structure is beneficial for bridging (Wu et al., 2016). Cyclodextrin shows good performance due to its unique hydrophilic outer surface and hydrophobic cavity structure, which includes α - cyclodextrin, β - cyclodextrin and γ - cyclodextrin. Among them, β - cyclodextrin is the most widely used because α - cyclodextrin has small cavity, which limits its application, while γ - cyclodextrin is expensive to produce. Sodium alginate has

strong flocculation performance because of the rich hydroxyl and carboxyl groups distributed on its chain (Liu et al., 2020a).

It has been proven that natural-based flocculants exhibit good flocculation performance, better biodegradability and less toxicity for clay minerals, but their active components biodegrade quickly and thus need high dosage. There are other drawbacks for natural polymers, such as carboxyalkyl chitosan is amphoteric but it suffers from high electrostatic repulsion against negatively charged particles existing in the wastewater (Yang et al., 2011), β -cyclodextrin is limited by its low molecular weight and charge density when used (Jiang et al., 2010).

Table 3. Natural polymers used for clay minerals removing

Flocculants	Type of flocculants	Flocculation medium	Reference
Dex-CS	Cationic	Kaolinite	(Zeng et al., 2019)
Starch	Cationic	Kaolinite, bentonite	(Ziolkowska and Shyichuk, 2011)
Guar gum	Cationic/Non-ionic	Bentonite	(Zhang et al., 2013)
Guar gum	Cationic	Bentonite	(Nakamura et al., 2020)
Extracellular polymers	Cationic/Anionic	Montmorillonite	(Tan et al., 2014)
CS	Non-ionic	Kaolinite, Illite, Montmorillonite	(Haufe et al., 2017)
Coconut cream casein	Non-ionic	Kaolinite	(Fatombi et al., 2011)
Pectin	Non-ionic	Kaolinite	(Ho et al., 2010)

3.3. Natural-based grafted polymers

Grafting is a practical method for overcoming these drawbacks in natural polymers. Therefore, sort of natural-grafted-synthetic polymers are proposed, combining the advantages of synthetic and natural polymers. In recent years, grafted flocculants with natural polysaccharides as a backbone have attracted considerable attention in the treatment of clay minerals. Table 3 summarizes the polymerization methods and flocculated medium of different polymeric flocculants.

Grafted polymers with abundant branched chains play an important role in the flocculation process of clay minerals and the electrical neutralization and adsorption bridging effect are significantly enhanced. Their high charge density not only elevates aggregation efficiency but also can resist high shear rates of the flocs (Wang et al., 2021). The grafting of flexible PAM onto the rigid polysaccharide backbones increases the chances of the flocculants approaching the contaminant particles, and thus improves the flocculant ability of polysaccharide. A cationic polyacrylamide flocculant (L-CPA) was synthesized via AM and DMC grafting to lignin, which was used for flocculation of kaolinite suspension (Fig. 7). Results showed that L-CPA can form octopus-like hydrophilic micelles by self-assembly in water and had excellent flocculation effect. The transmittance of kaolinite suspension can reach 90% in the pH range of 5-9, and a small dosage of L-CPA (4.0-4.5 mg/L) was needed (Chen et al., 2020b).

The traditional synthesis method uses a chemical free radical initiator such as ceric ammonium nitrate (CAN), ammonium persulfate (APS) and potassium persulfate (KPS) to generate free radical sites on the polymers' backbone, combined with monomers to form grafting chains (Razali et al., 2015; Tang et al., 2018). Till now, microwave radiation has been one of the most effective methods to synthesize grafted polymeric flocculants. It can greatly shorten reaction time via reducing the reaction-activation energy. Meanwhile, the diffusion effect of this technique can speed up the heat and mass transfer process and the synthesized flocculants can be used under a wide pH range. At present, microwave-assisted technique is more commonly used to initiate the grafting reaction, which involves a synergistic reaction between microwave radiation and chemical free radical initiation (Mittal et al., 2018; Zeng et al., 2019; Zhao et al., 2020).

3.4. Application of polymers in mineral processing

Due to the clay minerals act as gangue minerals in the most flotation systems, polymers are often used

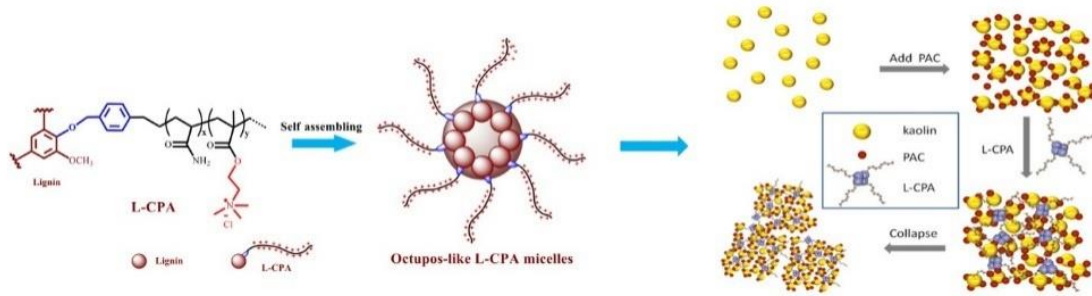


Fig. 7. Schematic diagram of synthesis and flocculation process of L-CPA (Chen et al., 2020b)

Table 4. Preparation methods and performance of representative grafted flocculants

Flocculants	Type of flocculants	Flocculation medium	Reference
Lignin-g-P(AM+DMC)	Cationic	Kaolinite	(Chen et al., 2020b)
Lignin-g-P(AM+DMC)	Cationic	Kaolinite & bentonite	(Hasan and Fatehi, 2018, 2019)
β -cyclodextrin-g-P(AM+DAC)	Cationic	Kaolinite & humic acid	(Liu et al., 2019b)
CS-g-P(AM+DAC)	Cationic	Bentonite & humic acid	(Wang et al., 2021)
CS-g-P(AM-IA)	Cationic	Kaolinite	(Liu et al., 2018)
Xylan-g-METAC (DMC)	Cationic	Kaolinite & bentonite	(Wang et al., 2016)
Starch-g-DADMAC	Cationic	Kaolinite	(Razali and Ariffin, 2015)
Starch-g-P(DMC+AM)	Cationic	Kaolinite	(Hu et al., 2020)
SA-g-PDMC	Cationic	Kaolinite & humic acid	(Liu et al., 2020b)
Cellulose-g-DMC	Cationic	Kaolinite	(Li et al., 2018)
Bamboo pulp cellulose-g-PAM	Cationic	Kaolinite	(Liu et al., 2014)
P(AM-HEC)	Anionic	Cu (II)	(Chaouf et al., 2019)
MCC(pAA-co-pDMC)	Amphoteric	Kaolinite	(Wang et al., 2019)
CMC-CTA	Amphoteric	Kaolinite	(Agbovi and Wilson, 2018)
AP-g-PAM	Amphoteric	Kaolinite	(Singh et al., 2013)
CMC-g-PAM	Amphoteric	Kaolinite	(Yang et al., 2012)
CNC-g-PDMA	Non-ionic	Kaolinite	(Liu et al., 2017)
Fenugreek gum-g-PAM	Non-ionic	Kaolinite & Coal fine	(Mishra and Kundu, 2019)
Guar gum-g-PAM	Non-ionic	Coal fine	(Sand and Kwark, 2017)

in mineral flotation to selectively separate useful substances from gangue minerals. Natural polymers such as polysaccharides show certain selectivity when used in mineral flotation (Jain et al., 2013; Kumar et al., 2018). In a recent report by Qian et al. (Qian et al., 2021), sodium polystyrene sulfonate (PSSNa) can be used as an effective inhibitor of titanite in ilmenite ore flotation, which has little effect on the flotation of ilmenite but has a strong inhibitory effect on ilmenite minerals. Although researchers have studied many polymers that selectively flocculate minerals, the non-selective adsorption of polymers on mineral particles is one of the main challenges and the main factor limiting industrial application in multicomponent ore system.

In aqueous solution, the properties of polymer often change due to the variation of solution environment. For example, with the change of temperature, polymers can show a sharp and rapid reversible hydrophilic and hydrophobic transformation. Poly(N-isopropyl acrylamide) (PNIPAM) is a well-known temperature-responsive polymer, and current temperature-responsive polymers are studied based on PNIPAM (Ng et al., 2018). The environment of wastewater produced by mineral

processing is complex and variable. It is required that the polymer used for wastewater clarification should have specific structure and properties.

Table 5. Polymers used in mineral processing

Flocculants	Type of flocculants	Flocculation medium	Reference
Starch	Non-ionic	Ore slimes	(Jain et al., 2013)
Dex-Tannin	Non-ionic	Fluorite	(Zhang et al., 2018)
CMC	Non-ionic	Ore slimes	(Kumar et al., 2018)
PSSNa	Anionic	Titanaugite	(Qian et al., 2021)
Guar gum	Non-ionic	Ore slimes	(Jain et al., 2017)
PNIPAM	Non-ionic	Kaolinite	(Li et al., 2007)
P(NIPAM-co-AA)	Anionic	Hematite	(Ng et., 2017)

3.5. Comparison between three types of polymers

Although the research of natural-based grafted flocculants has made great progress, compared with the traditional synthetic flocculants, the widespread use of natural-based grafted flocculants is limited by its high production cost. For example, the effective method of grafted flocculants synthesis is microwave-assisted polymerization, but this method requires high production costs. Therefore, the flocculant widely used in industry is still synthetic flocculant. The advantages and disadvantages of chemical synthetic, natural and grafted flocculants are listed in Table 4. Consequently, it is of great significance to discover a universal and suitable method for commercial applications.

Table 6. Advantages and disadvantages of three types of polymers

Flocculants	Advantages	Disadvantages
Synthetic flocculants	<ul style="list-style-type: none"> ● Low dosage ● Low cost ● High efficiency 	<ul style="list-style-type: none"> ● Residual monomers are toxic ● Non-biodegradable ● Instable under shearing
Natural flocculants	<ul style="list-style-type: none"> ● Non-toxic ● Biodegradable ● Inexpensive 	<ul style="list-style-type: none"> ● High dosage ● Lower efficiency
Natural-grafted flocculants	<ul style="list-style-type: none"> ● Eco-friendly ● High efficiency ● High molecular weight 	<ul style="list-style-type: none"> ● High production cost ● Complex synthesis process

4. Perspectives of polymeric flocculants of clay minerals

4.1. In-depth investigations of microscopic mechanism

At present, reported mechanisms of polymeric flocculants and suspended clay minerals in wastewater are focused on charge neutralization and bridging, and in a few cases, relied on sweeping and electrostatic patch (Sharma et al., 2006). As a summary, in the case of opposite charges between polymeric flocculants and adsorbents, charge neutralization is generally assumed as the main mechanism. Bridging occurs when the length of the flocculant molecule is large enough to exceed the effective range of repulsive forces between the clay particles in solution, resulting in the formation of a three-dimensional network of floc.

In addition to understanding the basic mechanism of interaction between flocculant molecules and clay mineral surfaces, it is of great significance to deeply explore the microscopic mechanism of interaction at atom/molecular level for the structural design of novel flocculants. Computer simulation is an effective way to investigate the microscopic mechanisms such as density functional theory (DFT) and molecular dynamics (MD) calculations. It can be concluded that the adsorption mechanism between polymeric flocculants and clay minerals is that the polymer chains are adsorbed to the surface of clay minerals via hydrogen bonding and electrostatic attraction interactions between

the Al-OH, Si-OH and polymers' functional groups (Nasser et al., 2013). For instance, the interaction mechanism between cationic PAM and the basal surfaces of kaolinite were the hydrogen bonds formed between the carbonyl oxygen atoms in PAM and the hydrogen atoms on the kaolinite surface, and between the quaternary ammonium head group of monomers and the surface oxygen atoms (Ren et al., 2020a). More information on reagent/polymer-clay mineral interactions is shown in Table 7 by DFT calculation. Molecular simulations can also be used to determine the ratio of the carbon atom skeleton in rings, columns and tails of polymer chains (Quezada et al., 2021), and to determine the synergies between natural polymer skeletons and synthetic polymers in the natural-based grafted polymers (Sun et al., 2020).

Table 7. DFT computed interaction of polymers and mineral surface

Polymer/Monomer Formula	Adsorbate	Adsorption Energy (kCal/mol)	Mode of Interaction	Reference
(Me ₂ N ⁺ Cl-CH ₂ CHOHCH ₂) _n	Kaolinite	-25.92	Hydrogen bonds (-OH in monomer with kaolinite)	Jacquet et al., 2018
(CH ₂ CHOH) _n	Kaolinite	-11.37		
CH ₂ CHCONH ₂	Kaolinite	-25.56	Hydrogen bonds (carbonyl oxygen in monomer with kaolinite)	Ren et al., 2020b
CH ₂ CHCOOH	Kaolinite	-22.63		
Me ₃ N ⁺ Cl-(CH ₂) ₂ OOCCHCH ₂	Kaolinite	-42.02	Electrostatic	Geatches et al., 2012
(CH ₃) ₃ N ⁺ Cl-(CH ₂) ₃ CH ₃	Kaolinite	-30.49		
(CO(CHOH) ₅) _n	Hematite	-70.67	Coordinate covalent bonds (Hydroxyl and carboxyl oxygen in CMC with hematite)	Kumar et al., 2018
(CO(CHOH) ₅) _n	Goethite	-27.28	Weak hydrogen bonds	
(CO(CHOH) ₅) _n	Gibbsite	-26.88	Weak hydrogen bonds	Jain et al., 2013
(CO(CHOH) ₅) _n	Kaolinite	-31.07	Weak hydrogen bonds	
(C ₆ H ₁₀ O ₅) _n	Hematite	-74.00	Strong Omolecule-Fe bonds	Lee et al., 2013
(C ₆ H ₁₀ O ₅) _n	Gibbsite	-11.00	Weak hydrogen bonds	
(C ₆ H ₁₀ O ₅) _n	Kaolinite	-11.00	Weak hydrogen bonds	Lee et al., 2013
(C ₆ H ₁₂ O ₆) _n	Kaolinite	-42.58	Hydrogen bonds (hydroxyl in kaolinite with β-D-glucose)	

4.2. Weaken or inhibit the hydration of clay minerals

On the basis of fully understanding the surface and interface properties of clay minerals, weakening or inhibiting the hydration of clay minerals is an effective approach to improve the flocculation efficiency. On the one hand, adding quaternary ammonium gemini surfactant can reduce clay minerals swelling (Murtaza et al., 2020). In a recent report, 2,3- epoxypropyl trimethyl ammonium chloride as an inhibitor has been studied to inhibit the hydration expansion of montmorillonite (Sun et al., 2021b). On the other hand, a polymer is designed so that the adsorption between the polymer and clay is enough to exclude the water molecules adsorbed on the clay surface, thus weakening the hydration of clay minerals. The results of weakening or inhibiting hydration can significantly reduce the thickness of hydration film on clay mineral surface, which is conducive to the direct contact between flocculant molecules and clay mineral surface, and the capture effect of fine clay minerals is obviously improved and also reduce the burden of subsequent flocculation dehydration.

4.3. Accurately control the interfacial properties of clay

The fine clay minerals in aqueous solution disperse stably under the influence of hydration repulsion and electrostatic repulsion between particles. The precise control of the interface of fine particles is of great significance to the flocculation of mineral particles. Polymeric flocculants with hydrophobic groups, for example, can alter particle forces, changing hydration repulsion into hydrophobic

attraction. Using an amphiphilic salt or hydrophobic modification can reduce the polymerization difficulty of synthesis of hydrophobic modified polymers and cause a surface-modification effect (Tang et al., 2021; Yang et al., 2020). Moderately hydrophobic polymeric flocculants with fine structural factors are expected to play an important role in the flocculation of fine clay particles that are difficult to settle (Gao et al., 2021; Hu et al., 2021).

4.4. Design novel flocculants based on the interfacial characteristics

The interfacial characteristics of clay minerals have high requirements on the structure of flocculants. Based on the interfacial characteristics of clay minerals, precise design of flocculant structure can be achieved through molecular structure optimization, and efficient flocculation of fine clay minerals can be realized.

5. Conclusions

In order to achieve high-efficiency, non-toxic, no secondary pollution, and low dose flocculation of fine clay minerals, it is necessary to design one or more efficient eco- friendly flocculants. The existing polymeric flocculants are designed based on molecular weight, charge density and spatial configuration of polymers. Under the condition of fully understanding the interfacial characteristics of clay minerals, the polymeric flocculants designed and synthesized according to their characteristics can effectively improve the flocculation effect.

The interfacial characteristics of clay minerals in aqueous suspension are complex, affected by water, pH and ion composition of the suspension. Hydration or swelling characteristic of clay-water, variable charges on the surface of clay particles in different pH and complicated ion composition have higher requirements for flocculants. While synthetic polymers, natural polymers and natural-based grafted polymers have distinct advantages, they all have certain drawbacks in their respective uses. To further improve the existing polymeric flocculants, it is important to conduct microscopic analysis of the interaction between polymers and clay minerals, overcome flocculation limitations, and optimize the polymers' structures.

In the treatment of clay minerals, the negative impact of chemical flocculants on the environment is a challenge in the treatment of clay minerals. As a result, biological flocculants such as bacteria are considered to be a viable alternative to chemical flocculants. It is another promising option for addressing the issue of chemical pollution. However, the production cost and extraction technique of biological flocculants still need to be solved.

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